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(54) NEEDLE MANGANESE COMPLEX OXIDE, PRODUCTION AND USE THEREOF

(57)Abstract:

PURPOSE: To obtain a new complex oxide by firing a mixture of manganese dioxide of γ -type crystalline structure with a Li compound and at least one of metallic materials selected from Ni, Co, Fe and Cr.

CONSTITUTION: Manganese dioxide of γ -type crystalline structure having a BET specific surface area of 150-500m², a lithium compound and at least one of metallic material selected from Ni, Co, Fe and Cr are mixed. This mixture is subjected to the first heat treatment at a temperature lower than 500°C in the air and/or oxygen for 10 or more hours, then to the second heat treatment at 500-850°C for 10 or more hours to give a manganese complex oxide of the formula: LiM_xMn_{2-x}O₄ (M is Ni, Co, Fe, Cr; 0.0<x≤0.5) having a spinel type crystalline structure, particles sizes of 10 or less μ m, a lattice constant of less than 8.24Å; and a BET specific surface area of 1 or more m²/g. This composite oxide is used as a positive electrode active substance, while Li or Li alloy is used as a negative electrode active substance to easily and inexpensively give a Mn-Li secondary cell using a non-aqueous electrolyte.

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 CLAIMS

[Claim(s)]

[Claim 1] The manganese multiple oxide to which it becomes from a particle with a particle size of 10 micrometers or less, and the crystal structure is a spinel type and a BET specific surface area is expressed $1\text{m}^2 / \text{above g}$ by chemical formula $\text{LiMX Mn}_{2-X}\text{O}_4$ (the inside M of a formula is at least one or more kinds chosen from nickel, Co, Fe, and Cr, and is $0.0 < x \leq 0.5$).

[Claim 2] The manganese multiple oxide according to claim 1 whose lattice constant is less than 8.24Å.

[Claim 3] The manufacture method of the manganese multiple oxide of the claim 1 characterized by calcinating the mixture of manganese dioxide and the lithium compound in which a BET specific surface area has gamma type crystal structure of $150\text{m}^2 / \text{g}$ to $500\text{m}^2 / \text{g}$, and at least one or more kinds of metallic materials chosen from nickel, Co, Fe, and Cr.

[Claim 4] The manufacture method of the manganese multiple oxide of a claim 4 that a lithium compound is characterized by being a lithium nitrate.

[Claim 5] The manufacture method of the manganese multiple oxide of a claim 4 that the metallic material of nickel, Co, Fe, and Cr is characterized by being those nitrates.

[Claim 6] The manufacture method of the manganese multiple oxide of the claim 4 characterized by performing 2nd heat treatment at 500-degree-C or more temperature of 850 degrees C or less in baking in the manufacture method of the manganese multiple oxide of a claim 3 after performing 1st heat treatment at the temperature of 500 degrees C or less.

[Claim 7] The lithium secondary battery characterized by using for a negative-electrode active material the compound which can occlusion emit a lithium, a lithium alloy, or a lithium, using nonaqueous electrolyte for an electrolyte, and using the manganese multiple oxide of a claim 1 for a positive active material.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] this invention is a thing about a new manganese multiple oxide, its manufacture method, and its use. in detail It consists of a particle with a particle size of 10 micrometers or less. a BET specific surface area 1m² / above g The crystal structure is a spinel type and it is chemical formula LiMX Mn₂-X O₄ (the inside M of a formula is at least one or more kinds chosen from nickel, Co, Fe, and Cr, and is 0.0 < x ≤ 0.5). The manganese multiple oxide expressed, It is related with the lithium secondary battery which uses the manufacture method and this manganese multiple oxide for a positive active material.

[0002] Since a manganese multiple oxide is cheap, abundant in the manganese of a raw material also in resources and still easier to compound, it is a material which attracts attention most in the positive-active-material material for lithium secondary batteries.

[0003] Since a lithium secondary battery can constitute the cell of high-energy density theoretically, the research and development which aimed at highly efficient-ization also including what was already put in practical use partly as a new style rechargeable battery which bears the next generation are furthered actively.

[0004]

[Description of the Prior Art] With the spread of a personal youth's cordless devices, it is small and lightweight and development of a lithium secondary battery with a high energy density is demanded strongly.

[0005] Recently, development of the lithium ion type rechargeable battery using the compound which can occlusion emit lithium ions, such as a carbonaceous material metallurgy group oxide, is positively furthered for the purpose of safety reservation, without using a lithium metal and a lithium alloy for a negative electrode.

[0006] For this reason, it is necessary for the positive active material to use the compound containing the lithium.

[0007] LiMO₂ in which a basic skeleton has the layer structure which a lithium and transition metals arranged regularly with rock salt structure as a compound which contained the lithium now The type oxide (M is transition metals here) attracts attention. Also in it, research and development are actively furthered including utilization in part from a lithium cobalt oxide (it being written as the following LiCoO₂) and a lithium nickel oxide (it being written as the following LiNiO₂) showing a 4V class cell voltage.

[0008] However, LiCoO₂ That it is related and a cobalt raw material is expensive and LiNiO₂ It is related and the trouble that composition is difficult is already pointed out.

[0009] As a material which shows a 4V class cell voltage in addition to the two above-mentioned material, it is the lithium manganese spinel (it is written as the following LiMn₂O₄) of a spinel type structure. It is known.

[0010] LiMn₂O₄ LiCoO₂ since composition is easy, and moreover abundant in manganese raw materials also in resources and cheap LiNiO₂ It is expected as a material to replace.

[0011] LiMn₂O₄ It is Spinel structure and a lithium is the compound of the normal-spinel type with which manganese occupied 16d site and oxygen occupied 32e site for the spinel 8a site.

[0012] In other words, it has the structure in which the lithium occupied one eighth of the tetrahedral sites of cubic-closest-packing oxygen, and manganese occupied one half of octahedral sites.

[0013] This LiMn₂O₄ When it uses for the positive active material of a lithium secondary battery, it is shown clearly that there are a field which functions on the voltage of about 4 V, and a field which operates on the voltage of about 3 V (135 or small ** et al., collection [of the 29th cell debate lecture summaries], and P1988).

[0014] In the field which functions on the voltage of about 4 V, it is LiMn₂O₄. The lithium ion in a crystal lattice moves through 16c site of an empty oxygen octahedral site in the lithium occupancy site in the crystal structure, and the reaction which goes in and out, without destroying structure where the cubic of the original skeletal structure is

maintained progresses.

[0015] On the other hand, in the field which functions on the voltage of about 3 V, it is LiMn_2O_4 . The reaction to which a lithium ion frequents 16c site of the oxygen octahedral site of the empty in a crystal lattice with the change to a tetragonal phase from the cubic of the crystal structure progresses.

[0016] In order to constitute a lithium secondary battery with an energy density high between the two above-mentioned reactions, it is important to use the field which shows the voltage of about 4 V.

[0017] It is LiMn_2O_4 in the field which shows the voltage of about 4 V. When it is made to function, as mentioned above, from a charge-and-discharge reaction progressing without change of crystal system, where the cubic structure of a basic skeleton is maintained, the reversible reaction was expected and the proposal of application to a lithium secondary battery has so far accomplished many.

[0018] However, a rechargeable battery with a high energy density cannot be constituted from an old proposal, and it has not yet resulted by utilization.

[0019] It is LiMn_2O_4 in the field which shows the voltage of about 4 V. Although a charge-and-discharge reaction progresses where cubic structure is maintained when it is made to function, although it is [some], expansion and contraction of a crystal lattice take place by the oxidation reduction of manganese, and receipts and payments of a lithium ion.

[0020] According to examination of this invention persons, it is LiMn_2O_4 . Although it is then gradually when the cycle of charge and discharge, i.e., the volume change by expansion and contraction of this crystal lattice, is repeated. The conductive fall accompanying decay of the local crystal structure, detailed-izing of a particle, and detailed-izing and the conductive fall considered to originate in a poor contact with electric conduction assistants (for example, acetylene black, graphite, etc.) further take place, and, for this reason, the fall of the capacity accompanying a charge-and-discharge cycle takes place.

[0021] Furthermore, it is LiMn_2O_4 in the field which shows the voltage of about 4 V when charge and discharge are performed at a high charge-and-discharge rate. Even if it has regulated discharge voltage so that it may be made to function, by repeating charge and discharge Reduction goes to the field which shows the voltage of about 3 V partly, the above-mentioned conductive fall is accelerated because transition of the crystal structure takes place, the utilization factor of a positive active material becomes uneven by the conductive fall of a positive electrode etc., and it is thought that reversibility falls remarkably.

[0022] The above reason to LiMn_2O_4 It is judged that it has not yet resulted by utilization.

[0023] As a method of solving this trouble, the way other elements replace some manganese is proposed.

[0024] For example, in JP,3-219571,A and JP,4-160769,A, $\text{LiX MY Mn (2-Y) O}_4$ ($0.85 \leq x \leq 1.15$, $0.02 \leq y \leq 0.5$) which replaced some manganese by at least one kind of Co, Cr, and Fe is proposed.

[0025] These proposals are replacing some manganese by Co, Cr, and Fe, are making a lattice constant small and making the crystal structure firmer, and aim at preventing destruction of the crystal structure, i.e., the fall of service capacity.

[0026] However, even if saying [making the crystal structure firmer] can make the flexibility over the volume change of the crystal lattice by the charge-and-discharge reaction able to fall and it can reduce degradation speed, the fall of service capacity is still difficult to protect.

[0027] Furthermore, by these proposals, since the particle of the compound which is compounding each at 900 degrees C and is obtained at this temperature was large, when it is used for a positive active material, detailed-ization of the particle by charge and discharge becomes easy to progress, and a capacity fall tends to take place.

[0028] On the other hand, in JP,5-36412,A, it has proposed being LiX Mn (2-X) O_4 which replaced some manganese by at least one kind of Fe and Cr (A being Fe and/or Cr, and $0.1 \leq X \leq 0.4$), in Fe, being 650 degrees C or more 800 degrees C or less, and heat-treating at 650-degree-C or more temperature of 850 degrees C or less in Cr.

[0029] However, by this proposal, it is Mn_2O_3 to a manganese raw material. According to [are using it and] examination of this invention persons, it is Mn_2O_3 . When using and compounding at the temperature of 650 degrees C or more, the particle diameter of the compound obtained is large, detailed-ization of the particle by charge and discharge becomes easy to progress, and a capacity fall tends to take place.

[0030] As mentioned above, LiMn_2O_4 proposed until now With the compound which replaced some manganese by other elements, it has not resulted in utilization the place which the cycle property at the time of using for the positive active material of a lithium secondary battery is inadequate, and is former.

[0031] On the other hand, with the spread of a personal youth's cordless devices, it is small and lightweight and development of a lithium secondary battery with a high energy density is demanded strongly.

[0032] By present, it is LiCoO_2 to a positive active material. Although the lithium secondary battery of the ion type

which used carbonaceous material for the negative electrode and used nonaqueous electrolyte for the electrolyte is put in practical use, in order to make it spread broadly as a noncommercial small power supply or an on-site type power supply for power storage, development of a cheaper and more stable lithium secondary battery is desired.

[0033]

[Problem(s) to be Solved by the Invention] The purpose of this invention is new LiMn_2O_4 . It is in offering the manganese system lithium secondary battery which proposed the compound which replaced some manganese by other elements, and its manufacture method, and used this compound for the positive active material further and which was excellent in the cycle property.

[0034]

[Means for Solving the Problem] As a result of this invention persons' inquiring wholeheartedly for the purpose of solving the above-mentioned technical problem, it consists of a new manganese multiple oxide, i.e., a particle with a particle size of 10 micrometers or less, and BET specific surface areas are more than $1\text{m}^2/\text{g}$. The crystal structure is a spinel type and it is chemical formula $\text{LiMX Mn}_2\text{XO}_4$ (the inside M of a formula is at least one or more kinds chosen from nickel, Co, Fe, and Cr). The manganese multiple oxide expressed with $0.0 < x \leq 0.5$ is found out for the first time. the manganese multiple oxide The BET specific surface area found out the thing which calcinate the mixture of manganese dioxide and the lithium compound which have gamma type crystal structure of $150\text{m}^2/\text{g}$ to $500\text{m}^2/\text{g}$, and at least one or more kinds of metallic materials chosen from nickel, Co, Fe, and Cr and for which thing composition can be carried out. Furthermore, it finds out that the manganese system lithium secondary battery which is not in the former and which was excellent in the cycle property can be constituted from using this for the positive active material of a lithium secondary battery, and came to complete this invention.

[0035]

[Function] Hereafter, this invention is explained concretely.

[0036] Chemical formula $\text{LiMX Mn}_2\text{XO}_4$ (the inside M of a formula is at least one or more kinds chosen from nickel, Co, Fe, and Cr, and is $0.0 < x \leq 0.5$) of this invention The manganese multiple oxide expressed is a manganese multiple oxide of Spinel structure to which at least one or more kinds of metals with which a lithium is chosen from manganese, and nickel, Co, Fe and Cr in one half of octahedral sites occupied one eighth of the tetrahedral sites of cubic-closest-packing oxygen.

[0037] The manganese multiple oxide of this invention is LiMn_2O_4 which the position of a diffraction peak shifted to the angle-of-elevation side. An analogous X diffraction pattern is shown. That is, a crystal lattice is LiMn_2O_4 . It is the manganese multiple oxide which became small.

[0038] According to examination of this invention persons, it is LiMn_2O_4 by the valence and ion size of a substitution metal. It becomes a manganese multiple oxide with a small crystal lattice.

[0039] When nickel replaces some manganese, since the stable phase as an oxide of nickel is NiO , nickel is replaced by some manganese as + divalent, it is that the + trivalent manganese in a compound oxidizes to + tetravalence, and contraction of a crystal lattice produces it.

[0040] When it replaces by Co, since the stable phase as an oxide of Co is CoO or Co_3O_4 , a part of Co replaces by some manganese as + trivalent as + divalent. + when the effect that + trivalent manganese oxidizes to + tetravalence when replacing as divalent replaces as + trivalent, the contraction which is a crystal lattice arises also in one of cases, and the case of both hybrid models according to the effect replaced by Co with an ionic radius smaller than manganese

[0041] the case where it replaces by Fe and Cr -- the stable phase as an oxide -- respectively -- Fe_2O_3 And Cr_2O_3 it is -- it replaces by some manganese as + trivalent from things, respectively Contraction of a crystal lattice arises according to the effect replaced by Fe and Cr with an ionic radius smaller than manganese.

[0042] By the above effect, a crystal lattice is LiMn_2O_4 . It is thought that it becomes small. Furthermore, the rate of contraction of the crystal lattice by the amount of substitution changes from the above thing with the kinds and the amounts of substitution of a metallic material to replace, respectively.

[0043] In addition, even if it is trespassing upon a lithium site, and + divalent when an ionic radius is too small, although there is a metal which forms a stable oxide with a metal with an ionic radius smaller than manganese, and + divalent besides nickel, Co, Fe, and Cr, when an ionic radius is too large, since a substitution reaction cannot occur easily, nickel, Co, Fe, and Cr which are proposed this time are considered to be the most excellent substitution metal.

[0044] For the manganese multiple oxide of this invention, a crystal lattice is LiMn_2O_4 . Although it is a small compound, a crystal lattice is with a bird clapper small, and is considered that there are the following effects. When making the amount of the + trivalent manganese in a compound decrease fundamentally and making it function on the voltage of about 4 V, the amount of replace [some manganese / by at least one kind of nickel, Co, Fe, and Cr] of the manganese which participates in an oxidation-reduction reaction decreases. In other words, a charge-and-discharge

reacting weight will be restricted, therefore the amount of expansion / contraction of a crystal lattice becomes small, and it is thought that a cycle property improves.

[0045] According to examination of this invention persons, some manganese by furthermore, the thing to replace by at least one kind of nickel, Co, Fe, and Cr If discharge voltage is regulated so that it may be made to function in the field which a charge-and-discharge reaction progresses uniformly by the whole active material, and shows the voltage of about 4 V even when the crystal structure becomes the compound which progressed uniformly and charge and discharge are performed at a high charge-and-discharge rate for this reason It comes to function in reversible, without a reduction reaction going to the field which shows the voltage of about 3 V.

[0046] As for the size of a crystal lattice, it is more desirable that it is 8.10Å or more in less than 8.24Å that it is less than 8.24Å desirable in more detail.

[0047] When the size of a crystal lattice uses for the positive active material of a lithium secondary battery in 8.24Å or more, expansion and contraction of the crystal lattice accompanying charge and discharge become large, and decay of the crystal structure promotes.

[0048] On the other hand, if a crystal lattice is less than 8.24Å, expansion and contraction of the crystal lattice accompanying charge and discharge will become small, and its cycle property will improve.

[0049] If a crystal lattice becomes not much small too much, since the diffusion within solid phase of a lithium will be in a difficult state, in connection with charge and discharge, destruction of a crystal lattice becomes easy to take place.

[0050] According to examination of this invention persons, when a high power type lithium secondary battery is constituted, it turns out that 8.10Å or more is desirable.

[0051] The amount of substitution at the time of replacing by at least one kind of nickel, Co, Fe, and Cr is chemical formula $\text{LiMX Mn}_{2-X} \text{O}_4$. It is indispensable that the value of X at the time of expressing is 0.5 or less or more in 0.0, and 0.2 or less are more desirable in more detail at 0.05 or more.

[0052] While the crystal lattice of the compound obtained becomes small too much as stated previously when the value of X exceeds 0.5, composition of the compound of spinel single phase becomes difficult.

[0053] Moreover, when it constitutes the lithium secondary battery of high capacity, since required, the thing for which both charge-and-discharge capacity and a cycle property are reconciled and which make the value of X 0.2 or less or more by 0.05 is more desirable.

[0054] The manganese multiple oxide expressed with chemical formula $\text{LiMX Mn}_{2-X} \text{O}_4$ (the inside M of a formula is at least one or more kinds chosen from nickel, Co, Fe, and Cr, and is $0.0 < x \leq 0.5$) of this invention makes it indispensable to consist of particles with a particle size of 10 micrometers or less.

[0055] Although it is unknown about a detail, since it is a particle with a particle size of 10 micrometers or less, when it uses for the positive active material of a lithium secondary battery, it becomes easy to absorb expansion and contraction of the crystal lattice accompanying charge and discharge between particles, and the conductive fall considered to originate in a poor contact with an electric conduction assistant can be suppressed.

[0056] Although it will not be restricted especially if it is 10 micrometers or less, when the restoration nature as a positive active material is taken into consideration, a particle diameter can maintain the restoration nature as a positive-electrode material with restricting to 10 micrometers from 1 micrometer, and a bird clapper to this range is desirable in composition of a high capacity type rechargeable battery being possible.

[0057] As for the size of the surface area of the manganese multiple oxide expressed with chemical formula $\text{LiMX Mn}_{2-X} \text{O}_4$ (the inside M of a formula is at least one or more kinds chosen from nickel, Co, Fe, and Cr, and is $0.0 < x \leq 0.5$) of this invention, a BET specific surface area makes it indispensable for a BET specific surface area to be more than $1 \text{ m}^2/\text{g}$.

[0058] Even when the value of a BET specific surface area used the compound 1 m^2 / more than g for the positive active material of a lithium secondary battery, and contact to an electric conduction assistant and the electrolytic solution becomes good and performs charge and discharge at a high charge-and-discharge rate, a charge-and-discharge reaction progresses uniformly by the whole active material, and the rechargeable battery which excelled [type / high capacity] in the cycle property can be constituted.

[0059] When the restoration nature as a positive active material is taken into consideration, the restoration nature as a positive-electrode material can maintain with restricting the value of a BET specific surface area to below $10 \text{ m}^2 / \text{g}$, the composition of a high capacity type rechargeable battery is attained, and especially between $5 \text{ m}^2 / \text{g}$ to $10 \text{ m}^2 / \text{g}$ is desirable.

[0060] In the manufacture method of the manganese multiple oxide of this invention, it is indispensable to use manganese dioxide in which a BET specific surface area has gamma type crystal structure of $150 \text{ m}^2 / \text{g}$ to $500 \text{ m}^2 / \text{g}$ as a source of manganese.

[0061] while a reaction progresses uniformly and particle growth is notably suppressed by using manganese dioxide in which a BET specific surface area has gamma type crystal structure of 150m² / g to 500m² / g as a source of manganese -- composition -- a uniform manganese multiple oxide becomes compoundable

[0062] Although the detail of mechanism ***** of this reaction is not clear, it thinks as follows. Since the surface area is very large, manganese dioxide in which the BET specific surface area used by this invention has gamma type crystal structure of 150m² / g to 500m² / g has very high reactivity with a lithium compound. Therefore, it is easy to generate the manganese multiple oxide of uniform composition.

[0063] Moreover, since manganese dioxide in which the crystal structure has the gamma type crystal structure has the channel structure of (1x2) and the diffusion path inside [of a lithium] a crystal is secured, when it is made to react with a lithium compound, it is thought that a reaction advances easily. Furthermore, although the reason is unknown, since the surface area is very large, it is thought that composite-ization with a metallic material also advances easily and the manganese multiple oxide of uniform composition tends to generate it.

[0064] This effect has a remarkable BET specific surface area from 150m² / g to 500m² / g. This is considered to be ***** by the following reason.

[0065] It becomes difficult for a BET specific surface area to be unable to perform sufficiently uniformly mixture with manganese dioxide, a lithium compound, and a metallic material, but to manufacture the manganese multiple oxide of uniform composition by under 150m² / g.

[0066] the case where a BET specific surface area exceeds 500m² / g -- the way of the heat phase transition of manganese dioxide -- a composite-ized reaction with a lithium compound and a metallic material -- happening -- being easy -- since the channel structure which that it is easy (1x2) diffuses [a lithium] can distort -- a composite-ized reaction -- progressing -- being hard -- while it becomes difficult to manufacture the manganese multiple oxide of uniform composition -- condensation of a particle -- happening -- being easy -- a manganese multiple oxide 10 micrometers or less cannot be

[0067] Since it stated above, if a BET specific surface area uses for the source of manganese manganese dioxide which has gamma type crystal structure of 150m² / g to 500m² / g, it will be thought that a manganese multiple oxide with uniform composition can be manufactured easily.

[0068] Manganese dioxide in which the BET specific surface area used by this invention has gamma type crystal structure of 150m² / g to 500m² / g can be manufactured by the thing which is shown in JP,41-1696,B and which perform an electrolysis reaction with the usual sulfuric-acid concentration higher than the manufacture conditions and the usual high current density of an electrolytic manganese dioxide so that it may be.

[0069] On the usual manufacture conditions, an electrolytic manganese dioxide deposits in the shape of an anode plate by the oxidation reaction shown in (1) formula.

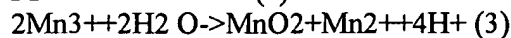
[0070]



For this reason, after an electrolysis end, although trituration processing is performed and it considers as a style or manganese at the shape's of a particle after exfoliating from an anode plate, the BET specific surface areas of manganese dioxide obtained by this method are below 100m² / g.

[0071] On the other hand, manganese dioxide of gamma type crystal structure used by this invention makes only Mn³⁺ ion an anode plate product, as it is making high sulfuric-acid concentration in the electrolytic solution, the stability of Mn³⁺ ion is made to increase and it is shown in (2) formulas rather than the manufacture conditions of the usual electrolytic manganese dioxide, and it is (3) in the electrolytic solution. It is manufactured by making the adding-water decomposition reaction shown by the formula perform.

[0072]



By the above-mentioned method, manganese dioxide in which a BET specific surface area has gamma type crystal structure of 150m² / g to 500m² / g can be manufactured.

[0073] What thing may be used for them as long as the lithium material used for manufacture of the manganese multiple oxide of this invention is a lithium and/or a lithium compound. For example, although a lithium metal, a lithium hydroxide, a lithium oxide, a lithium carbonate, an iodation lithium, a lithium nitrate, an oxalic acid lithium, an alkyl lithium, etc. are illustrated, especially a lithium nitrate is more desirable preferably also what is fused at the temperature of 500 degrees C or less, and in it.

[0074] What thing may be used for them as long as the metallic materials used for manufacture of the manganese multiple oxide of this invention are a metal and/or metallic compounds. For example, although the hydroxide of a metal

and a metal, a metal oxide, a metal carbonate, a metal nitrate, an organometallic complex, etc. are illustrated, especially a metal nitrate is more desirable preferably also what is fused at the temperature of 500 degrees C or less, and in it.

[0075] Especially the mixed method of manganese dioxide and the lithium compound in which a BET specific surface area has gamma type crystal structure of 150m² / g to 500m² / g, and at least one or more kinds of metallic materials chosen from nickel, Co, Fe, and Cr is not restricted, and should just be mixed by solid phase and/or the liquid phase. For example, the method of mixing the powder of the above-mentioned raw material with dry type and/or wet and the method of mixing because a BET specific surface area adds and agitates manganese dioxide which has gamma type crystal structure of 150m² / g to 500m² / g in the solution which dissolved and/or suspended the lithium compound and the metallic material are illustrated. Manganese dioxide and the lithium compound in which a BET specific surface area has gamma type crystal structure of 150m² / g to 500m² / g, The baking method of the manganese multiple oxide which calcinates the mixture of at least one or more kinds of metallic materials chosen from nickel, Co, Fe, and Cr Although not restricted especially, after calcinating the 1st heat treatment at the temperature of 500 degrees C or less in the atmosphere and/or oxygen, it is desirable to perform 2nd heat treatment at the temperature of 850 degrees C or less more than the temperature exceeding 500 degrees C.

[0076] According to examination of this invention persons, by the low temperature side, a composite-ized reaction progresses bordering on 500 degrees C, and development of Spinel structure takes place by the elevated-temperature side. Therefore, after fully advancing a composite-ized reaction with the 1st heat treatment first, by performing a crystal-growth reaction with the 2nd heat treatment, composition is more uniform and the manganese multiple oxide from which Spinel structure developed can be compounded. Furthermore, a composite-ized reaction is promoted more by performing 1st heat treatment in the atmosphere and/or oxygen.

[0077] In addition, it is desirable to carry out below 850 degrees C from a bird clapper at the temperature at which the 2nd heat treatment exceeds 850 degrees C that particle growth and the reduction reaction of manganese tend to occur.

[0078] In addition, although not restricted especially concerning a firing time, the 1st heat treatment and the 2nd heat treatment of 10 hours or more are desirable.

[0079] As a negative electrode of the lithium secondary battery of this invention, the compound which can occlusion emit a lithium metal, a lithium alloy, or a lithium can be used. As a lithium alloy, a lithium / tin alloy, a lithium/aluminium alloy, a lithium/lead alloy, etc. are illustrated, for example. moreover -- as the compound which can occlusion emit a lithium -- carbonaceous material, such as graphite and a graphite, FeO and Fe 2O₃, and Fe 3O₄ etc. -- an iron oxide, CoO and Co 2O₃, and Co 3O₄ etc. -- oxides, such as cobalt oxide, are illustrated

[0080] Moreover, the electrolyte of the lithium secondary battery of this invention Although not restricted especially, for example Carbonate, such as a propylene carbonate and diethyl carbonate Lactone, such as sulfolanes, such as a sulfolane and dimethyl sulfoxide, and gamma-butyrolactone In at least one or more kinds of ether, such as dimethoxyethane, of organic solvents What dissolved at least one or more kinds of lithium salt, such as a lithium perchlorate, 4 fluoride lithium borate, a 6 fluoride [phosphoric-acid] lithium, and a trifluoromethane sulfonic-acid lithium, the solid electrolyte of lithium ion conductivity of an inorganic system and an organic system, etc. can be used. It used for the manganese multiple-oxide positive active material obtained by this invention, and the cell shown in drawing 1 was constituted.

[0081] The lead wire for 1:positive electrodes, the mesh for 2:positive-electrode current collection, 3:positive electrode, 4:separator, 5:negative electrode, the mesh for 6:negative-electrode current collection, the lead wire for 7:negative electrodes, and 8:container are shown all over drawing.

[0082] this invention is not limited by these examples although an example is shown as an example of this invention below.

[0083]

[Example] In addition, X diffraction measurement in the example and the example of comparison of this invention, observation of a particulate structure, and measurement of specific surface area were performed by the following methods.

[0084]

X diffraction measurement : Measurement model The Mac Saiensu-Sha Co., Ltd. make MXP3 An irradiation X-ray Cu K alpha rays Measurement mode Step scan Scanning conditions As 2theta, 0.04 degrees Measurement time 5 seconds Measuring range It is 10 degrees to 70 degrees as 2theta. Observation of a particulate structure : [Measurement model] A scanning electron microscope JEOL JSM-T220A Acceleration voltage 15kV Surface-area measurement : Measurement model BET adsorption method specific-surface-area measuring device measuring method Inside of a nitrogen gas air current (the rate of flow : per minute 15 millimeter RITTO RU) Automatic, after processing at 250

degrees C for 40 minutes Surface-area measuring device (ASAmade from Shibata science machine industrial , Inc.- 2000) It measured.

[0085] Moreover, the length of a crystallographic axis is the X diffraction measurement data of each compound to the WPPD method (Whole-Powder-Pattern Decomposition Method). It determined.

[0086] Furthermore, the component analysis was measured by the ICP AEM method.

[0087] [Manufacture of a manganese multiple oxide]

As example 1 (manufacture of $\text{LiCo}_{0.1}\text{Mn}_{1.9}\text{O}_4$) example 1, it is $\text{LiCo}_{0.1}\text{Mn}_{1.9}\text{O}_4$. It manufactured by the following methods. Pt board is used for an anode plate in the solution which contains a manganese sulfate in 25g [l.] /, and contains a sulfuric acid by the concentration of 150g/l., and it is 50 A/dm². The particle-like electrolytic manganese dioxide was obtained by electrolyzing with current density. This electrolytic manganese dioxide was manganese dioxide with 190m² of BET specific surface areas / g, 1 micrometer or less of particle diameters, and the gamma type crystal structure as a result of analysis.

[0088] Next, this manganese dioxide, lithium-nitrate (special grade chemical), and cobalt-nitrate 6 hydrate (special grade chemical) After mixing so that Li:Mn:Co may be set to 1:1.9:0.1 by the mole ratio, it calcinated at the temperature of 450 degrees C in the atmosphere for 24 hours.

[0089] Next, after lowering this to a room temperature and grinding and mixing with a mortar, it calcinated at the temperature of 650 degrees C in the atmosphere for 24 hours.

[0090] The observation result of a particulate structure was shown in drawing 3 , and a chemical-analysis result, the length of a crystallographic axis, and the measurement result of a BET specific surface area were shown for the X diffraction pattern of the obtained compound in Table 1 at drawing 2 .

[0091]

[Table 1]

	化学組成	a 軸の長さ (Å)	B E T 比表面積 (m ² / g)	容量維持率 (%)
実施例 1	$\text{LiCo}_{0.1}\text{Mn}_{1.9}\text{O}_4$	8.227	8.5	95
実施例 2	$\text{LiCo}_{0.2}\text{Mn}_{1.8}\text{O}_4$	8.219	9.0	98
実施例 3	$\text{LiNi}_{0.1}\text{Mn}_{1.9}\text{O}_4$	8.235	8.3	96
実施例 4	$\text{LiFe}_{0.1}\text{Mn}_{1.9}\text{O}_4$	8.238	7.8	95
実施例 5	$\text{LiCr}_{0.2}\text{Mn}_{1.8}\text{O}_4$	8.237	8.2	96
比較例 1	$\text{LiCo}_{0.2}\text{Mn}_{1.8}\text{O}_4$	8.222	0.6	90

[0092] As a result of analysis, for the obtained compound, it consists of grains 5 micrometers or less, and the length of a crystallographic axis is $\text{LiCo}_{0.1}\text{Mn}_{1.9}\text{O}_4$ of 8.227Å, and 8.5m² of BET specific surface areas / g. It turns out that it is the manganese multiple oxide of the Spinel structure expressed.

[0093] It manufactured like the example 1 except having mixed as example 2 (manufacture of $\text{LiCo}_{0.2}\text{Mn}_{1.8}\text{O}_4$) example 2, so that Li:Mn:Co might be set to 1:1.8:0.2 by the mole ratio.

[0094] The obtained compound was a manganese multiple oxide of Spinel structure which consists of a particle 5 micrometers or less as a result of analysis.

[0095] A chemical-analysis result, the length of a crystallographic axis, and the measurement result of a BET specific surface area were shown in Table 1.

[0096] As example 3 (manufacture of $\text{LiNi}_{0.1}\text{Mn}_{1.9}\text{O}_4$) example 3, it is $\text{LiNi}_{0.1}\text{Mn}_{1.9}\text{O}_4$. It manufactured by the following methods. After mixing nickel nitrate 6 hydrate (special grade chemical) with manganese dioxide manufactured in the example 1, and a lithium nitrate (special grade chemical) so that Li:Mn:nickel may be set to 1:1.9:0.1 by the mole ratio, it calcinated at the temperature of 450 degrees C in the atmosphere for 24 hours.

[0097] Next, after lowering this to a room temperature and grinding and mixing with a mortar, it calcinated at the

temperature of 650 degrees C in the atmosphere for 24 hours.

[0098] As a result of analysis, the obtained compound consists of a 5-micrometer particle, and the length of a crystallographic axis is $\text{LiNi}_{0.1}\text{Mn}_{1.9}\text{O}_{4.0}$ of 8.235A, and 8.3m^2 of BET specific surface areas / g. It turns out that it is the manganese multiple oxide of the Spinel structure expressed. A chemical-analysis result, the length of a crystallographic axis, and the measurement result of a BET specific surface area were shown in Table 1.

[0099] As example 4 (manufacture of $\text{LiFe}_{0.1}\text{Mn}_{1.9}\text{O}_4$) example 4, it is $\text{LiFe}_{0.1}\text{Mn}_{1.9}\text{O}_4$. It manufactured by the following methods. After mixing nine hydrates (special grade chemical) of iron nitrate with manganese dioxide manufactured in the example 1, and a lithium nitrate (special grade chemical) so that Li:Mn:Fe may be set to 1:1.9:0.1 by the mole ratio, it calcinated at the temperature of 450 degrees C in the atmosphere for 24 hours.

[0100] Next, after lowering this to a room temperature and grinding and mixing with a mortar, it calcinated at the temperature of 850 degrees C in the atmosphere for 24 hours.

[0101] As a result of analysis, the obtained compound consists of a particle 10 micrometers or less, and the length of a crystallographic axis is $\text{LiFe}_{0.1}\text{Mn}_{1.9}\text{O}_{4.0}$ of 8.238A, and 7.8m^2 of BET specific surface areas / g. It turns out that it is the manganese multiple oxide of Spinel structure expressed.

[0102] A chemical-analysis result, the length of a crystallographic axis, and the measurement result of a BET specific surface area were shown in Table 1.

[0103] As example 5 (manufacture of $\text{LiCr}_{0.2}\text{Mn}_{1.8}\text{O}_4$) example 5, it is $\text{LiCr}_{0.2}\text{Mn}_{1.8}\text{O}_4$. It manufactured by the following methods. After mixing nine hydrates (special grade chemical) of a chromium nitrate with manganese dioxide manufactured in the example 1, and a lithium nitrate (special grade chemical) so that Li:Mn:Cr may be set to 1:1.8:0.2 by the mole ratio, it calcinated at the temperature of 450 degrees C in the atmosphere for 24 hours.

[0104] Next, after lowering this to a room temperature and grinding and mixing with a mortar, it calcinated at the temperature of 850 degrees C in the atmosphere for 24 hours.

[0105] As a result of analysis, the obtained compound consists of a particle 10 micrometers or less, and the length of a crystallographic axis is $\text{LiCr}_{0.2}\text{Mn}_{1.8}\text{O}_{4.0}$ of 8.237A, and 8.2m^2 of BET specific surface areas / g. It turns out that it is the manganese multiple oxide of the Spinel structure expressed.

[0106] A chemical-analysis result, the length of a crystallographic axis, and the measurement result of a BET specific surface area were shown in Table 1.

[0107] As an example 1 of example of comparison 1 (manufacture of $\text{LiCo}_{0.2}\text{Mn}_{1.8}\text{O}_4$) comparison, it is $\text{LiCo}_{0.2}\text{Mn}_{1.8}\text{O}_4$. It manufactured by the following methods. After mixing Mn 3O4 (trimanganese tetroxide : special grade chemical) and basic cobalt carbonate (special grade chemical) with a lithium carbonate (special grade chemical) so that Li:Mn:Co may be set to 1:1.8:0.2 by the mole ratio, it calcinated at the temperature of 900 degrees C in the atmosphere for 10 hours. The observation result of a particulate structure was shown in drawing 4, and a chemical-analysis result, the length of a crystallographic axis, and the measurement result of a BET specific surface area were shown for the X diffraction pattern of the obtained compound in Table 1 at drawing 2. As a result of analysis, for the obtained compound, a length of one side consists of a regular-octahedron needlelike particle 1 micrometers or more, and the length of a crystallographic axis is $\text{LiCo}_{0.2}\text{Mn}_{1.8}\text{O}_{3.8}$ of 8.222A **. Although it turns out that it is the manganese multiple oxide of the Spinel structure expressed, BET specific surface areas were 0.6m^2 / g.

[0108] It is the mixture (tradename : TAB- 2) of the polytetrafluoroethylene of an electric conduction agent, and acetylene black about the manganese multiple oxide manufactured in [composition of cell] examples 1-5, and the example 1 of comparison. It mixed at a rate of 2:1 by the weight ratio. It is 75mg of mixture 1 ton/cm2 At a pressure, it is the mesh (SUS 316) of 20mmphi. After casting in the shape of a pellet upwards, reduced-pressure-drying processing was performed at 200 degrees C for 5 hours.

[0109] This is used for the positive electrode of 3 of drawing 1, the piece of a lithium clipped out from the lithium foil (0.2mm in thickness) is used for the negative electrode of 5 of drawing 1, and it is a lithium perchlorate to propylene carbonate in the electrolytic solution 1 mol/dm3 What was dissolved by concentration is infiltrated into the separator of 4 of drawing 1, and it is 2 the cross section of 2.5cm. The cell shown in drawing 1 was constituted.

[0110] The cell created by the [evaluation of cell performance] above-mentioned method is used, and it is 1.0 mA/cm2. With fixed current, the cell voltage repeated charge and discharge between 4.5V and 3.5V.

[0111] It was shown in Table 1, the rate, i.e., the capacity maintenance factor, of the service capacity of 50 cycle eye to the service capacity of 1 cycle eye.

[0112] Although each manganese multiple oxide manufactured in the examples 1-5 showed 95% or more of high maintenance factor, the manganese multiple oxide manufactured in the example 1 of comparison was 90%. A result is shown in Table 1.

[0113]

[Effect of the Invention] As stated above the manganese multiple oxide of the invention in this application It consists of a particle with a particle size of 10 micrometers or less. a BET specific surface area 1m² / above g Chemical formula $\text{LiMX Mn}_{2-x}\text{O}_4$ (the inside M of a formula is at least one or more kinds chosen from nickel, Co, Fe, and Cr) of a spinel type [crystal structure] $0.0 < x \leq 0.5$ It is the new manganese multiple oxide expressed, and if the new manganese multiple oxide is used for a positive electrode, the manganese system lithium secondary battery which is not in the former and which was excellent in the cycle property can be constituted.

[0114] It is useful knowledge on industry to have found out a manganese system positive-electrode material applicable to a lithium secondary battery positive active material.

[Translation done.]